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B. T. GALLOWAY, *Chief of Bureau.*

SOME EFFECTS OF REFRIGERATION ON SULPHURED AND UNSULPHURED HOPS.

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Drug-Plant, Poisonous-Plant, Physiological, and Fermentation Investigations.

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LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Bureau of Plant Industry,
Office of the Chief,
Washington, D. C., September 18, 1912.

Sir: I have the honor to transmit herewith and to recommend for publication as Bulletin No. 271 of the series of this Bureau a manuscript by Dr. W. W. Stockberger, Physiologist, and Mr. Frank Rabak, Chemical Biologist, entitled "Some Effects of Refrigeration on Sulphured and Uusulphured Hops," submitted by Dr. R. H. True, Physiologist in Charge of the Office of Drug-Plant, Poisonous-Plant, Physiological, and Fermentation Investigations.

In this paper is discussed some of the changes which occur in important constituents of hops under different conditions of storage and a comparison is made of the relative efficacy of certain methods for preventing undesirable changes in hop constituents.

This bulletin shows that both refrigeration and sulphuring retard changes in the volatile constituents of hops and that the determination of the value of hops from the aroma varies according to individual preference for or dislike of one or the other of the aromatic constituents. The conclusions drawn from a comparison of valuations made from both physical and chemical standpoints will be of practical importance to all interested in the hop industry.

Respectfully,

B. T. Galloway,
Chief of Bureau.

Hon. James Wilson,
Secretary of Agriculture.

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SOME EFFECTS OF REFRIGERATION ON SULPHURED AND UNSULPHURED HOPS.

INTRODUCTION.

Opinions are greatly divided as to the desirability or general expediency of the practice of treating hops with the fumes of burning sulphur during the process of drying. This process, which in the United States is termed "sulphuring," has been long in vogue and has come to be regarded as an essential part of the method of preparing hops for market. The use of sulphur as an adjunct to hop drying apparently originated in England and from the first was regarded as a more or less effective means of checking the tendency of newly packed hops to heat and spoil in the bale. Later, other virtues were claimed for sulphuring in addition to that of preservative action, and those who advocate the use of sulphur now believe that it favorably affects the hops by changing and improving the color, by hastening the drying through causing the rapid death of the cells, and by preventing fermentation, thereby improving the keeping qualities.

Aside from sulphuring, a number of other expedients have been resorted to for the purpose of delaying or retarding the changes which normally occur in the chemical constituents of hops after they have been dried and baled. Of these expedients refrigeration is the most widely used and from many considerations it is perhaps the most efficient and generally satisfactory method of preservation that has as yet been employed.

The sulphuring of hops is such a common practice in the United States that practically all hops placed in cold storage may be regarded as having absorbed a varying quantity of sulphurous acid, depending to a certain extent upon the quantity of sulphur used at the time of drying. Since both sulphuring and cold storage are held to be efficient agents in retarding changes in the essential constituents of hops, the diminished rate of deterioration of sulphured hops in cold storage must be due to the combined action of these two processes. However, the relative efficacy of these two processes,

or the extent to which the one or the other alone would accomplish the desired result, is usually a subject of approximate estimation only.

For the purpose of obtaining some experimental data upon the preservative action on hops of sulphuring and cold storage, singly and in combination, suitable material was prepared and held under observation for several years. The results of this study, which are given in some detail in this bulletin, indicate that both cold storage and sulphuring tend to delay certain undesirable chemical changes and that the usual trade judgment can not always be relied upon to give an accurate measure of the extent to which these changes have occurred. However, it is fully realized by the writers that further experimentation is necessary before the conclusions drawn from this work can be considered to have a general application.

PREPARATION OF THE HOPS STUDIED.

The hops which furnished the materials for the observations here recorded were all picked from the same part of a field on a hop ranch in the Sacramento Valley on August 30, 1907, and were dried on the same day under the senior writer's supervision. As the hops were received from the field they were equally distributed to two duplicate stove kilns until each had received a load of about 4,500 pounds, green weight. The fires were lighted and the temperature of each kiln was gradually raised to a point between 130° and 140° F., between which limits it was maintained until the drying was completed. On one of these kilns 110 pounds of sulphur was burned under the hops during the drying, which required 13 hours; on the other kiln no sulphur was used and the time required for drying was 18 hours. The dry hops from each of these two kilns were separately deposited in the cooling room and on September 2 two bales of the usual commercial type were prepared from the unsulphured hops and two from those which had been heavily sulphured. These four bales were conveyed to Sacramento, where two bales, one of sulphured and one of unsulphured hops, were placed in cold storage at 36° F. in the hop storeroom of the Buffalo Brewing Co., and the two remaining bales, one of which was sulphured and one unsulphured, were placed in ordinary storage in the Clunie warehouse.

PHYSICAL CHANGES IN THE HOPS IN COLD AND IN ORDINARY STORAGE.

As a rule, it is difficult to correlate the valuation of hops as determined from their physical characters with the indications of their value derived from chemical analysis. In the present case, however,

some chemical determinations were made which are not ordinarily taken into account in analyzing hops, and the results furnish some interesting parallels when compared with the relative rank in quality of the four bales of hops as fixed by physical valuation.

In order to have the differences in physical condition expressed in the language of the trade and as nearly as possible from the trade viewpoint, samples were drawn from time to time from the four bales and submitted to various trade experts, who were asked to report their impressions as to the general condition and relative merit of the various samples.

Early in April, 1908, after the hops had been in storage for seven months, samples were drawn from each of the four bales and submitted to five trade experts, all of whom concurred in the following report made by one of their number:

> We have examined these samples as to their condition at the present time to see if there was any difference between cold and regularly stored hops, and we are of the same opinion that there is no difference between the cold-stored and regularly stored hops.

The bales were not sampled a second time until midsummer, and during the time which had elapsed since the first sampling the hops in ordinary storage had been subject to the influence of the hot and dry weather which prevails in the Sacramento Valley at this season of the year. Naturally, it was expected that at this time certain differences would be apparent in the hops under different conditions of storage. On July 24, 1908, samples were drawn and submitted to an expert hop buyer, who reported on them as follows:

Unsulphured cold-stored hops.—Fine fresh hop flavor; good oily feeling; aroma almost as good as new hops and seems to be about the same as that of the sulphured cold-stored hops.

Sulphured cold-stored hops.—Fine fresh hop flavor; good oily feeling; aroma almost as good as new hops, but color somewhat lighter than the color of the unsulphured sample above described.

Unsulphured ordinary-stored hops.—Flavor decidedly that of old hops as compared with the cold-stored samples; feeling dry; lupulin not very sticky; color about the same as the color of the unsulphured sample above.

Sulphured ordinary-stored hops.—Fine fresh flavor; good oily feeling; aroma almost as good as new hops, but the color somewhat lighter than the color of the unsulphured sample above described.

At this time it is decidedly noticeable that the cold-stored hops have by far the best flavor and that they feel almost as oily as new hops, while the ordinary-stored hops are becoming poorer.

This judgment was taken within an hour after the bales had been sampled, and on coming into the room where the samples had been placed I thought that the excellent aroma was due to new hops. I was really surprised at the great difference in the aroma between the ordinary-stored and cold-stored hops, but

on comparing color I can not notice any serious difference between sulphured and unsulphured hops in either case.

These same samples were next submitted to a second expert, who made the following statement:

The difference between the ordinary-stored and the cold-stored hops is now very noticeable. The unsulphured cold-stored sample has a very good flavor and looks fresh and bright. The unsulphured ordinary-stored sample has not such a good flavor as the former, is very much drier, and is becoming rapidly aged. The difference between these two is particularly noticeable in the appearance of the sides of the samples, the side of the cold-stored sample showing up much brighter and fresher than that of the other.

The sulphured cold-stored sample has a fine fresh flavor and is a particularly well-kept hop, while the sulphured ordinary-stored sample has a musty, old flavor and is rather dried out. The difference between these two samples is not so much in the appearance as in the aroma.

On the day following, these samples were submitted to a brewmaster, who delivered the following opinion:

The cold-stored hops have a lighter color as compared with the ordinary-stored hops, the lupulin is bright and shiny, the hops have a very oily and sticky feeling, and the aroma is almost like that of new hops.

The ordinary-stored hops have a dull, dry color; the lupulin is not so bright and appears to be hard and dry, with very little oil as compared with the cold-stored hops; the flavor is decidedly different and very much like that of old hops.

The bales were not sampled again until February 13, 1909, eighteen months after they were first placed in storage. The samples drawn on this date were first submitted to the brewmaster previously mentioned, and his judgment as to their relative merit was stated thus:

The sulphured and unsulphured cold-stored samples are respectively superior in flavor to the corresponding ordinary-stored samples. The sulphured samples in cold and ordinary storage are far superior both in flavor and color to the unsulphured samples.

The samples were next submitted to a trade expert, who gave the following opinion:

There is a very great difference between the cold-stored and ordinary-stored hops. The cold-stored samples are much brighter in appearance, have much more flavor, contain much more moisture, and their lupulin is much brighter than the ordinary-stored samples. The cold-stored samples would pass for new hops, while the ordinary-stored samples show their age and could not pass for anything else than "olds." By new hops I mean the 1908 crop.

Of the cold-stored hops the unsulphured sample seems to have a trifle more flavor than the sulphured one, but the latter has a sweeter flavor, which I believe would be preferred. The lupulin in both these samples is very fresh and moist, but that in the sulphured sample is a trifle the brighter. The sulphured sample, though in appearance fresher than the unsulphured sample, is not as moist as the latter.

Of the ordinary-stored hops the unsulphured sample has much more flavor than the sulphured sample, the latter having very little flavor at all. The

lupulin in the sulphured sample is a trifle brighter than that in the other. The unsulphured sample is much more moist than the sulphured sample, though the latter, before a detailed examination, appears to be the fresher of the two, a condition that can be traced to the brightening effect of the sulphur.

Since the sulphured cold-stored hops naturally conformed most closely in appearance and general condition to the hops usually found in the trade it was expected that they would be ranked first in quality, and such proved to be the case when the several expressions of judgment by the trade experts were analyzed. With respect to the other lots of hops, however, opinion was divided and the usual differences in trade judgment of quality are here well illustrated. The rank in order of merit as fixed by four of the judges was as follows:

Sulphured cold-stored hops	1,	1,	1,	1.
Unsulphured cold-stored hops	2,	2.	3,	2.
Sulphured ordinary-stored hops	3.	4.	2,	4.
Unsulphured ordinary-stored hops	4.	3.	4,	3.

CHANGES IN THE VOLATILE CONSTITUENTS OF HOPS IN COLD AND IN ORDINARY STORAGE.

On September 10, 1909, portions of the four bales of hops under consideration were withdrawn from storage and subjected to steam distillation to remove the volatile oils, which were then dried and purified and later examined to determine their degree of acidity and ester content. These factors, together with the percentage of yield of volatile oil, are given in Table I.

TABLE I.—*Comparison of volatile oils from sulphured and unsulphured hops in cold and in ordinary storage for two years.*

Source of oil examined.	Percentage of oil.	Acid number.	Ester number.
Sulphured cold-stored hops	0.12	7.3	78
Unsulphured cold-stored hops	.12	9.0	102
Sulphured ordinary-stored hops	.06	12.5	96
Unsulphured ordinary-stored hops	.05	15.6	151

An inspection of this table reveals the following interesting facts:

(1) The yield of oil is twice as great in the cold-stored hops as in those in ordinary storage.

(2) The acidity of the oil from the cold-stored hops is far less than that of the hops in ordinary storage.

(3) The oil from the sulphured hops in ordinary storage shows an increase of 71.2 per cent in acidity over that from the hops in cold storage, while the oil from the unsulphured hops in ordinary storage shows an increase of 73.3 per cent in acidity over that of the oil from those in cold storage.

(4) The oil from the unsulphured cold-stored hops shows an increase of 23.2 per cent in acidity over that from the hops that were sulphured, while the oil from the unsulphured, ordinary-stored hops shows an increase of 24.8 per cent in acidity over that from the hops that were sulphured.

(5) The oil from the unsulphured ordinary-stored hops shows an increase of 113.6 per cent in acidity over the oil from sulphured cold-stored hops.

(6) The ester content of the oil from the sulphured hops is much less than that of the oil from the unsulphured hops.

(7) The oil from the unsulphured ordinary-stored hops shows an increase of 23 per cent in ester content over that from the hops in cold storage, while the oil from the unsulphured hops in ordinary storage shows an increase of 46.6 per cent in ester content over the oil from those in cold storage.

(8) The oil from the unsulphured cold-stored hops shows an increase of 32 per cent in ester content over the oil from the sulphured cold-stored hops, while the oil from the unsulphured ordinary-stored hops shows an increase of 57.2 per cent in ester content over that from the sulphured hops in ordinary storage.

(9) The oil from the unsulphured ordinary-stored hops shows an increase of 93.5 per cent in ester content over that of the oil from the sulphured cold-stored hops.

This analysis gives an index of the relative efficacy of sulphuring and cold storage in controlling changes in acidity and ester content of the hop oils during the first two years of storage. The percentages of increase in acidity as between cold and ordinary storage are approximately three times the corresponding increase as between the sulphuring and nonsulphuring. This would apparently indicate that cold storage is three times as effective as sulphuring in retarding increase in acidity. With respect to ester content, the increase, as between the oils from cold and ordinary stored hops, is twice as great in unsulphured as in sulphured hops; also as between sulphured and unsulphured hops the increase in the ester content of the oil is twice as great in ordinary storage as in cold storage. This would seem to show that cold storage and sulphuring are about equally effective in retarding the increase in the ester content and that the two combined exert double the effect of either acting alone.

On December 1, 1910, fifteen months later, a second set of samples was taken from the four bales in storage and the volatile oils removed by distillation. The results of the examination of these oils, which are given in Table II, show little harmony with those of the first analysis.

TABLE II.—*Comparison of volatile oils from sulphured and unsulphured hops in cold and in ordinary storage for three years and three months.*

Source of oil examined.	Acid number.	Ester number.
Sulphured cold-stored hops	30.8	129.5
Unsulphured cold-stored hops	33.1	126.1
Sulphured ordinary-stored hops	24.0	105.0
Unsulphured ordinary-stored hops	24.0	109.0

An inspection of the table shows in this case the following relations:

(1) The acidity of the oil from the cold-stored hops is greater than that of the oil from the hops in ordinary storage.

(2) The acidities of the oils from the hops in ordinary storage are the same.

(3) The oils from the unsulphured cold-stored hops are highest in acidity.

(4) The ester content of the oils from the cold-stored hops is greater than that of the oils from the ordinary-stored hops.

(5) The oils from the sulphured hops in cold storage are highest in ester content.

(6) The oils from the unsulphured hops in cold and in ordinary storage, respectively, are higher in ester content than the oil from the sulphured hops in ordinary storage.

It is now evident that the apparent effects of sulphuring and cold storage as shown by the second analysis are almost the reverse of those indicated by the first analysis. How these seeming discrepancies may be harmonized can be seen from an inspection of Table III, in which the results of the two analyses are directly compared.

TABLE III.—*Comparison of the acidity and ester content of the oils from sulphured and unsulphured hops in cold and in ordinary storage.*

Kind of storage.	Sulphured hops.						Unsulphured hops.					
	Acid number.		Percentage of increase, 1910.	Ester number.		Percentage of increase, 1910.	Acid number.		Percentage of increase, 1910.	Ester number.		Percentage of increase, 1910.
	1909	1910		1909	1910		1909	1910		1909	1910	
Cold	7.3	30.8	321.9	78	129.5	66.0	9.0	33.1	267.4	103	126.1	22.4
Ordinary	12.5	24.0	92.0	96	105.0	9.3	15.6	24.0	53.8	151	109.0	7.7

Regarding, first, the acidity, the data in this table show that the percentage of increase in acidity was least in the oils from the hops which yielded oils that were highest in acidity in 1909 and greatest

in those lowest in acidity in 1909. Further, all the percentages of increase in acidity in 1910 are inversely proportional to the acidities in 1909. It is evident from the first analysis that the rate of change in the volatile constituents under consideration was greatest in the oils from the unsulphured hops in ordinary storage. These changes would continue until a maximum was reached, after which, owing to the interaction between the oxidation products of the various organic constituents of the hops and to the direct loss through volatilization, a decline in acidity would be the normal result. Assuming that this maximum was reached between the time of the first and the second analysis and applying this explanation to the data on acidity in Table III, the oils from the hops in ordinary storage may be regarded as having passed the maximum and as being in the declining phase with respect to acidity. Since the changes in the unsulphured hops in ordinary storage were not artificially retarded, the oils from these would naturally be nearer than the others to the maximum acidity at the time of the first analysis, and hence the percentage in increase in 1910 would be smallest.

Of the hops in cold storage, the oils from those that were unsulphured may be regarded as being at or near the maximum of acidity in 1910, thus accounting for the high figure of actual acidity and for the relatively large percentage of increase in acidity during this year. On the other hand, the oils from the sulphured cold-stored hops had apparently not reached the maximum acidity in 1910, owing to the slower rate of change in acidity in these oils due to the combined effect of sulphuring and cold storage. When viewed from this standpoint, the apparent discrepancy between the two analyses disappears and the balance of evidence is in favor of the conclusion (1) that under the four conditions of this experiment the acidity of the oil of hops increases to a maximum and then declines; (2) that sulphuring and cold storage merely retard but do not inhibit changes in acidity; and (3) that sulphuring and cold storage combined are more effective in retarding changes in acidity than either alone.

With respect to the esters, the data indicate that, in general, the changes in ester content have been similar to the changes in the acidity, although complicated by some other factors which make the relations of these changes to the conditions of storage less clear. The first analysis shows that the greatest changes in ester content occurred in the oils from the unsulphured hops and also that the oils from the hops in ordinary storage had undergone a greater change than the corresponding oils from the sulphured and unsulphured hops, respectively, in cold storage. It is possible that the

sulphur inhibits the development of ester beyond a certain point, in which case two maxima might be expected—one for the oil from sulphured hops and a higher one for the oil from unsulphured hops. The data of Table III agree with this assumption, for it appears that the oils of the unsulphured ordinary-stored hops were at or near the maximum of ester content in 1909, which thereafter rapidly declined, as shown by the figure reached in 1910.

The oil from the unsulphured cold-stored hops, which was below the probable maximum of ester content at the time of analysis in 1909, shows an apparent increase of 22.4 per cent in 1910; but, since the figure reached in 1910 is less than the probable maximum as indicated by the ester content of the oils from the hops in ordinary storage in 1909, it seems evident that the oils in the hops in cold storage had reached the maximum and entered upon the declining phase before the analysis in 1910. This view receives further support from the fact that the oil from the sulphured cold-stored hops, in which the chemical changes were most retarded, was higher in ester content in 1910 than the oil from those which were unsulphured.

The oils of the sulphured hops in ordinary storage appear to have passed their maximum of ester content and to be in the declining phase in 1910, while those of the hops that were sulphured and which show the greatest increase in ester content in 1910 appear to be at or near their maximum. The conclusions which are to be drawn with respect to the ester content, therefore, are that sulphuring retards the increase in ester content and inhibits it beyond a certain maximum, that cold storage retards but does not inhibit increase in ester content, and that sulphuring and cold storage combined are more effective in retarding changes in ester content than either alone.

CHANGES IN THE HOP RESINS.

In further pursuance of the plan of securing trade opinions with respect to the changes which had taken place in the four bales of hops under different conditions of treatment, portions of these bales were sent to a firm which is a large consumer of hops, with the request that the content of soft and hard resins be determined in each. The first analysis was made by the chemist of this firm in January, 1910, two years and four months after the bales had been first placed in storage. One year later a second lot of samples was sent to the same chemist and by him duly analyzed. The results of these two analyses are given in Table IV.

TABLE IV.—*Changes in resin content in sulphured and unsulphured hops in cold and in ordinary storage.*

Previous treatment of the hops analyzed.	Percentage of resins.					
	Soft resins.		Hard resins.		Total resins.	
	1910	1911	1910	1911	1910	1911
Sulphured, cold stored	10.5	10.3	5.5	5.6	16.0	15.9
Unsulphured, cold stored	10.6	8.7	5.3	6.2	15.9	14.9
Sulphured, ordinary stored	9.9	7.5	5.5	7.5	15.4	15.0
Unsulphured, ordinary stored	9.9	7.8	7.0	6.4	16.9	14.2

The figures in the foregoing table give an index to the changes which occurred in the resin content of these hops during the third year of storage. The slightest change in total resins, 0.1 per cent, took place in the sulphured cold-stored hops, while the greatest change, 2.7 per cent, is evident in the unsulphured hops in ordinary storage. The loss in soft resins was least in the sulphured cold-stored hops, 0.2 per cent, and greatest in the sulphured ordinary-stored hops, 2.4 per cent. The loss in soft resins of the unsulphured hops was 1.9 per cent in cold storage and 2.1 per cent in ordinary storage. As far as the evidence from these analyses goes, it indicates that sulphuring diminishes the loss of total resins, but does not diminish the loss of soft resins except when followed by cold storage. The greatest loss in soft resins was in the sulphured hops in ordinary storage, and, since the soft resins alone are intrinsically valuable, from this standpoint these hops must be regarded as the poorest of the lot. With respect to these particular samples, the balance of evidence indicates that there is a distinct advantage in both sulphuring and cold storage. However, the margin of difference in the results of the analyses is relatively small, and if the soft resins were regarded as the only measure of value, the advisability of incurring the expense of long-continued cold storage might be questioned.

PHYSICAL AND CHEMICAL VALUATION COMPARED.

Great difficulty is experienced not only in harmonizing the results of the physical and chemical estimations of the value of hops, as pointed out on a previous page, but also in bringing into accord the different individual judgments of quality, determined on a purely physical basis. This point has been discussed at some length in a previous publication [1] and will not be dwelt upon here further

[1] Stockberger, W. W. The Necessity for New Standards of Hop Valuation. Circular 33, Bureau of Plant Industry, U. S. Dept. of Agriculture. 1909.

than to state that it is well-nigh impossible to find two persons who will assign the same rank in value to six samples of commercial hops selected at random. Some light is thrown on these differences in judgment by a study of the different opinions rendered as to the relative value of the four lots of hops, all from the same source but subject to different conditions of treatment and storage. In order to bring out clearly some of the contrasts in these opinions, a table was prepared in which the physical and chemical valuations are compared. In this table the relative rank given each lot of hops by the four expert judges is indicated by the corresponding numeral.

The relative rank in acidity of the oils, which is similarly indicated, was determined from the results of the first analysis, since this analysis was made nearest in point of time to the physical valuations. The hops having the oils lowest in acidity were given the highest rank, those with oils next in acidity second rank, and so on, this order being determined by the fact that the hops having oils lowest in acidity had changed least from the original condition at the time of first storage. The relative rank with respect to ester content was determined in the same manner. The relative rank with respect to resins was determined from the content of soft resins, as these alone are considered to be the only resins of value in the utilization of hops. Since keeping quality, as indicated by a slow rate of change in the chemical constituents, is an important factor of value it was made the basis of relative rank in this case rather than the absolute quantity of soft resin. This relative keeping quality was determined from the difference in the content of soft resins, as shown by the two analyses. A direct comparison of all these relative rankings may be made from Table V.

TABLE V.—*Comparisons of rankings in value of sulphured and unsulphured hops in cold storage and in ordinary storage.*

Previous treatment of the hops.	Rank in value determined as noted.						
	By trade experts.				By acidity.	By ester content.	By keeping quality of soft resins.
	A.	B.	C.	D.			
Sulphured, cold stored	1	1	1	1	1	1	1
Unsulphured, cold stored	2	2	3	2	2	3	2
Sulphured, ordinary stored	3	4	2	4	3	2	4
Unsulphured, ordinary stored	4	3	4	3	4	4	3

From this table it appears that the rankings as to value are consistent in one case only, that of the sulphured cold-stored hops. However, on taking the judgments of the trade experts singly, that of expert A will be seen to agree with the rankings determined by

acidity, that of expert C with the rankings with respect to ester content, while the rankings of experts B and D agree with the order determined by the keeping quality of the soft resins. The reason for the differences in the judgments, based largely, if not entirely, upon the flavor or aroma of the hops, seems to lie, in part at least, in the difference of degree of sensitiveness of the individual to the several volatile constituents, which together form the aroma. It is well known that odors which are agreeable to some persons affect others unfavorably, and there is every reason to believe that in the present case the differences in judgment were due to the physiological idiosyncrasies of the observers. That this point of view is coming into wider recognition is shown by the following statement made by Dr. Albert Fischer:

> The determination of aroma is an entirely individual matter, depending upon the individual taste, the state of health, and the eventual influence of outside flavors on the person testing.[1]

However, since the number of individuals who passed judgment upon the experimental samples was small, the decisions rendered are not necessarily conclusive and certainly do not prove that the aroma should not be used as a factor in the determination of the value of hops. That the aroma is useful in determining the age and soundness of hops is conceded even by those who hold that it is not a proper factor from which to determine intrinsic value. The term "age" may be used to express the time that has elapsed since the hops were harvested or, in a relative sense, to denote the extent to which unfavorable changes have occurred in the hops. The hops under discussion here were of the same actual age, but owing to the different conditions of treatment they were of different relative ages, as shown by the different points to which the changes in the chemical constituents had progressed at the time of analysis. From the several classifications shown in Table V it is evident that the relative age and degree of deterioration as determined from analysis will depend very largely upon which one of the various constituents is selected as the basis of comparison. Similarly, the estimation of age or deterioration from the impressions produced by the aroma will vary according to the individual peculiarities of taste or fancy possessed by the observer. It is much to be regretted that there is not a better understanding of the relations between the factors commonly considered in establishing the relative market value of hops and the actual value of the hops in the processes in which they are utilized. The determination of a definite basis of value from which sound standards could be derived would have great practical importance, both for the producers and for the consumers of hops.

[1] Fischer, A. Modern methods of hop analysis. Letters on Brewing, vol. 11, 1912, p. 317.

GENERAL SIGNIFICANCE OF THE RESULTS.

The material which furnished the basis for the observations discussed in this paper was prepared primarily with the view to determining the feasibility of abandoning the practice of sulphuring hops. Some previous experiments had shown[1] that under certain conditions there was some danger of hops becoming slightly contaminated with arsenic during the process of sulphuring, to obviate which the discontinuance of the use of sulphur was naturally suggested. It was expected that the unsulphured hops would be received with less favor by the trade than those which had been sulphured, owing to the more pronounced variations in the color of the former, but at the time the bales of hops selected for observation were placed in storage the difference in general appearance was comparatively small, although the sulphured hops could be readily distinguished by their more uniform and somewhat brighter color. A study of the trade opinions rendered on these hops after they had been for some time in storage apparently shows that the difference in appearance due to sulphuring becomes accentuated with age and that the preference is for the sulphured hop.

When freshly cured, the difference in color between sulphured and unsulphured hops is, as a rule, much more pronounced; and, however careful the grower might be to harvest his crop at the stage of maturity best calculated to give the greatest uniformity in color, it is evident that in marketing his product he would have to seek for those consumers who have a preference for the greenish grades of hops.

From the results of the chemical tests it is apparent that unsulphured hops are less suited to the requirements of the consumer than those that have been sulphured, especially when they are stored for a considerable length of time before they are used. However, the fact should not be lost sight of that these tests were made on hops which had been in storage for more than two years, and the changes observed are certainly considerably greater than those which occur in hops which have been stored for a shorter period. Nevertheless, the greater part of the changes in certain constituents takes place during the first year of storage, as has been shown by Heron[2] in the case of the tannin of hops. But from the work of Moser,[3] who found that the tannin content of unsulphured samples was consistently smaller than that of sulphured samples of the same sorts, it is evident that the oxidation of the tannin is retarded by sulphuring. It may

[1] Stockberger, W. W. The sources of arsenic in certain samples of dried hops. Bulletin 121, pt. 4, Bureau of Plant Industry, U. S. Dept. of Agriculture. 1908.

[2] Heron, John. The tannin of hops. Journal of the Federated Institutes of Brewing, vol. 2, 1896, p. 172.

[3] Cited by Braungart in Der Hopfen, Munich, 1901, p. 849.

be safely assumed, however, that sulphuring is an effective means of retarding chemical changes in hops from the time they are cured until they have reached the desirable limit of age, usually determined by commercial conditions, provided such hops are held in cold storage.

It is fully realized that the conclusions drawn in this paper are subject to the criticism that the analyses are too few in number and that they are not coordinate in point of time with each other and with the physical valuations. Certain obstacles encountered in the course of the work made it impossible to round out the results as fully as was desired, yet it is believed that the coordinations suggested by the facts developed are of sufficient importance to justify this somewhat incomplete presentation, which should be regarded more as a report of progress than as an attempt at a full elucidation of the problem, for which much further experimentation is necessary.

SUMMARY.

Material for a comparative study of the effects of cold and ordinary storage on sulphured and unsulphured hops was secured from a hop field in the Sacramento Valley, Cal. The green hops were divided into two lots, only one of which was sulphured during the process of drying. Bales from each lot were placed in cold and in ordinary storage, and samples from these bales were drawn from time to time for examination with respect to physical condition and certain chemical constituents.

At intervals of 7 and 18 months, respectively, from the time the hops were placed in storage, samples were drawn and submitted to trade experts, who were asked to rate the samples according to their relative quality. All agreed that the sulphured hops in cold storage were best in quality, but opinion was divided as to the relative merit of the three other lots.

Determinations were made of the acidity and ester content of the volatile oils extracted from samples of the hops under each condition of storage. The conclusions drawn from these analyses are that both sulphuring and cold storage retard changes in the hops leading to an increase in acidity and ester content of the oils. Cold storage is apparently more effective than sulphuring in retarding the increase in acidity, but is less efficient than sulphuring in retarding increase in ester content. Cold storage and sulphuring combined are much more effective in retarding changes in acidity and ester content than either alone.

The percentage of decrease in the content of soft resins was less in the cold-stored hops than in those in ordinary storage. The evidence from the analyses goes to show that the sulphuring tends to

retard changes in the content of soft resins only when combined with cold storage.

Trade experts to whom samples of the hops under consideration were submitted for physical judgment differed widely in their opinions of relative merit, except in the case of the sulphured cold-stored hops, which all agreed ranked first. The relative rank in merit as determined from each of the factors sought in analysis was found to give corresponding differences. A comparison of these differences in the physical and chemical valuations shows that the determination of the value of hops from the aroma depends upon the personal taste of the observer and is greatly affected by the individual's preference or dislike of one or the other of the several constituents of the aroma.

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